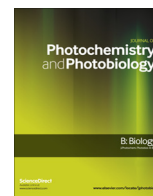




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## Photocatalytic synthesis of anilides from nitrobenzenes under visible light irradiation: 2 in 1 reaction

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## ABSTRACT

An efficient method has been developed for the synthesis of a series of anilides *via* a two in one reaction of nitrobenzenes with anhydride in the presence of TiO<sub>2</sub> as a nanocatalyst and photocatalyst under sunlight or blue LED irradiation. In this method simultaneously, nitrobenzenes convert to the corresponding anilines *via* photocatalytic reduction on the TiO<sub>2</sub> surface, and a condensation of aniline with the anhydride performed on the Lewis acid site of the TiO<sub>2</sub> surface. Interestingly amidation step leads to the promotion of better reaction and good selectivity in reduction of nitrocompounds. This method is simple, rapid, high yield, and green.

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## 1. Introduction

Anilide and its derivatives occupy pivotal positions in organic synthesis and synthesis of biologically and pharmaceutically active compounds [1–4]. Generally, the amides are produced through the reaction of a carboxylic acid or ester with an amine. Lately, one-pot reaction has become one of hot topics in green chemistry because it eliminates isolation of unstable intermediates and reduces waste production [5–8]. The conversion of nitroarenes to their corresponding acetanilides in a one-pot reaction is an important transformation in organic chemistry. As nitrobenzenes are readily available industrial chemicals, it is more efficient to start directly from the nitrocompound rather than to start from the corresponding amine or isocyanate [9]. In general, direct conversion of nitroarenes to acetanilides are carried out by iron powder with acetic acid [10], Pt nanoparticle ZrO<sub>2</sub> and acetic anhydride [11], molybdenum hexacarbonyl/acetic acid [12], and also anilides have been obtained either *via* nickel [13] or rhodium [14] or platinum [15] catalyzed carbonylation of nitroarenes. However, 50–100 atm CO required in each case.

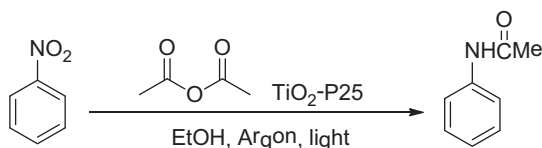
In the last decades, the increasingly serious energy crisis has led to an aggressive search for conversion of light energy into chemical energy by photocatalysis processes [16–25]. The Design of heterogeneous photocatalysis systems that encourage efficient one-pot synthesis is currently the focus of attention [26]. Photocatalyst

TiO<sub>2</sub> is able to promote two different transformations in one-pot by employing both photocatalytic and catalytic actions.

Lately, some successful examples of photocatalytic reduction of nitro compounds have been reported. TiO<sub>2</sub> [27–29], and N-doped TiO<sub>2</sub> [30], have been investigated for the reduction of nitrobenzenes to their corresponding anilines under UV light irradiation. On the other hand, CdS/graphene [31,32], dye-sensitized TiO<sub>2</sub> P25 [33,34], and PbBiO<sub>2</sub>X [35] have been employed to reduce these molecules by visible light irradiation. Shiraishi et al. reported one-pot synthesis of benzimidazoles and imines by simultaneous photocatalytic and catalytic reactions on Pt@TiO<sub>2</sub> nanoparticles [26,36]. Also, Sa et al. reported one-pot photo-reductive N-alkylation of aniline and nitroarene derivatives with primary alcohols over Au–TiO<sub>2</sub> [37]. Considering that the solar energy is an endless resource, recently significant progresses have been seen in heterogeneous photocatalysis for the synthesis of organic compounds using sunlight. Swaminathan et al. reported one-pot photocatalytic syntheses of benzimidazoles and indazole by Pt–TiO<sub>2</sub>, Ag–TiO<sub>2</sub>, and TiO<sub>2</sub>-P25 nanoparticles under UV and sunlight [38,39]. Lately our group have reported on activated amorphous TiO<sub>2</sub> coated into periodic mesoporous organosilicas (PMOs) [40], TiO<sub>2</sub>-N doped [41], β-Cyclodextrin/TiO<sub>2</sub> [42], and CdS [43,44] as efficient photocatalysts for synthesis of selective organic transformation under visible light. Moreover, we have reported that TiO<sub>2</sub>-P25 showed selectivity of over 80% for reduction of a series of nitrobenzenes under sunlight and LED irradiation [45]. TiO<sub>2</sub>-P25, which is frequently used as a standard in heterogeneous photocatalysis, consists of a mixture of anatase (75%) and rutile (25%) phases. The junction between anatase and rutile phases in TiO<sub>2</sub>-P25 exhibit high rate of the charge separation in comparison to pure phases.

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**Table 1**Photosynthesis of N-phenylacetamide from nitrobenzene and acetic anhydride in the presence of TiO<sub>2</sub>-P25 under sunlight and blue LED irradiation

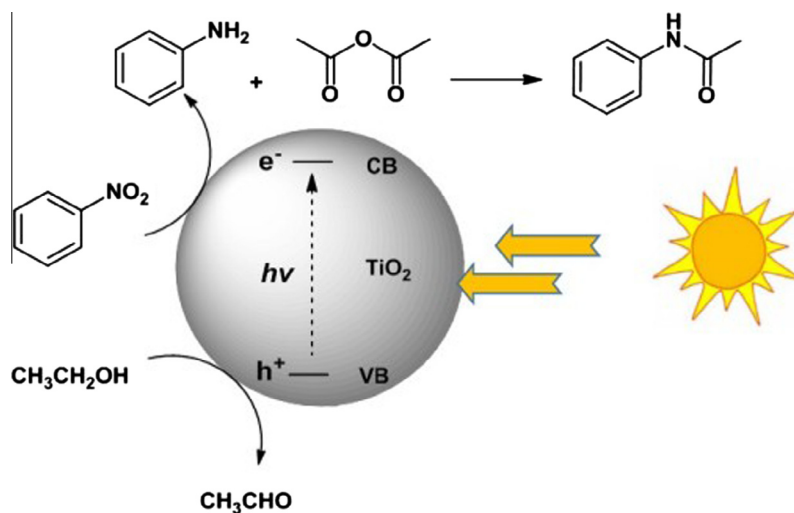
Entry	Nitrobenzene (mmol)	Acetic anhydride (mmol)	TiO <sub>2</sub> (g)	EtOH (ml)	Light	Time (h)	Conversion (%)	Select (%) <sup>a</sup>
1	0.02	0.022	0.01	4	☀	1	100	100
2	0.05	0.052	0.03	10	☀	2	100	100
3	0.1	0.12	0.05	20	☀	4	100	100
4 <sup>b</sup>	0.02	0.022	-	4	-	10	10	
5 <sup>c</sup>	0.02	0.022	0.01	4	-	10	80	
6 <sup>d</sup>	0.05	0	0.03	10	☀	4	100	55
7	0.002	0.0025	0.08	4	LED	30	100	100
8	0.005	0.0055	0.1	4	LED	48	35	18
9 <sup>d</sup>	0.002	0	0.08	4	LED	30	100	70

<sup>a</sup> Reaction conditions room temperature (25–35 °C) and sunlight irradiation (intensity = 90–100 × 10<sup>3</sup> lux). Selectivity =  $c_p/(c_{i0} - c_r)$  100%,  $c_{i0}$ : the initial concentration of nitrobenzene;  $c_r$ : the concentration of nitrobenzene during the reaction;  $c_p$ : the concentration of the product during the reaction. GC yield based on an internal-standard method.

<sup>b</sup> Aniline with acetic anhydride in the absence of TiO<sub>2</sub>.

<sup>c</sup> Aniline with acetic anhydride in the presence of TiO<sub>2</sub>.

<sup>d</sup> Reduction of nitrobenzene to aniline in the absent the acetic anhydride.

**Scheme 1.** Synthesis of N-phenylacetamide from nitrobenzene and acetic anhydride using TiO<sub>2</sub>-P25 under visible light.

Also, the rutile phase for TiO<sub>2</sub>-P25 acts as an antenna to extend the photoactivity into visible wavelengths [45,46].

## 2. Experimental

Photocatalytic reactions were carried out in a round bottom Pyrex flask and irradiated using four high power blue light LEDs 3 W lamp or by solar light under magnetic stirring at room temperature. Reaction conditions with solar light: the aromatic nitro compounds (0.05 mmol) and anhydride (0.052 mmol) were carried out in the presence of TiO<sub>2</sub>-P25 (0.03 g) in EtOH (10 mL) and irradiated under sunlight for 1–4 h. Reaction conditions with blue LED irradiation: aromatic nitro compounds (0.002 mmol) and anhydride (0.0025 mmol) were carried out in the presence of TiO<sub>2</sub>-P25 (0.08 g) in EtOH (4 mL), and irradiated by four high power blue light LEDs 3 W lamp for 30 h. While stirring, the mixture

became heterogeneous as the reaction progressed. The product yields were determined by gas chromatography monitoring. The structure of products were confirmed by NMR (see ESI<sup>1</sup>).

## 3. Results and discussion

In continuation of our work on visible light photoreduction of nitroaromatic compounds using sunlight and blue LED irradiation [45], in order to develop and improve this method, we present a strategy for one-pot synthesis of anilides using nitrobenzenes and anhydride as the reactants and TiO<sub>2</sub>-P25 nanoparticles as a heterogeneous catalyst at room temperature under visible photoirradiation. According to the best of our knowledge, the pho-

<sup>1</sup> † Electronic Supplementary Information.

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